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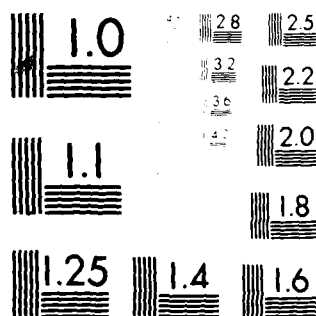
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For the period ending: April 30, 1982

CHEMICAL DURABILITY IMPROVEMENT AND STATIC FATIGUE OF GLASSES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
Series of investigations were made on the relation between the surface conditions of high silica glass and its mechanical strength. It was found that, 1) Heavy alkaline-earth elements such as Sr Ba in alkaline solutions tend to deposit on the silica glass surface and produce severe surface cracks, reducing the mechanical strength. 2) Surface energy of the glass appears to determine the mechanical strength of high silica glass. 3) Dissolution rate of high silica glass in water increases with increasing hydrostatic pressure. This appears inconsistent with the stress-corrosion theory. 4) Crack blunting		

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20. (continued) of high silica glass involves dissolution and precipitation process. 5) Surface condition of high silica glass influences the stress-rate dependence of the mechanical strength.

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## I. SUMMARY

Series of investigations were made on the relation between the surface conditions of high silica glass and its mechanical strength. It was found that

- 1) Heavy alkaline-earth elements such as Sr Ba in alkaline solutions tend to deposit on the silica glass surface and produce severe surface cracks, reducing the mechanical strength.
- 2) Surface energy of the glass appears to determine the mechanical strength of high silica glass.
- 3) Dissolution rate of high silica glass in water increases with increasing hydrostatic pressure. This appears inconsistent with the stress-corrosion theory.
- 4) Crack blunting of high silica glass involves dissolution and precipitation process.
- 5) Surface condition of high silica glass influences the stress-rate dependence of the mechanical strength.

## II. RESEARCH AND RESULTS

1. There are numerous inhibitors which, when placed in aqueous solution, can reduce the corrosion rate of glass. Alkaline earth elements such as Ca is an extremely effective inhibitor to the glass corrosion by alkaline solution. It was found, in the course of investigation of this inhibitor action of various ions, that heavy alkaline earth ions such as Sr and Ba produce severe surface cracks. This drastically reduces the mechanical strength of glass. (Appendix A)
2. Mechanical strength of high silica glass was measured in various liquids and was found to vary widely. This mechanical strength was found to correlate reasonably well with the surface energy of the glass estimated from the swelling of porous high silica glass. This observation appears to support Orowan's theory of environmental effect of mechanical strength rather than the stress corrosion theory which appears widely accepted. (Appendix B)
3. The popular explanation of the environmental effect (fatigue) on the strength of glass is by the stress corrosion mechanism. This mechanism assumes that the corrosion of glass increases with tensile stress. However, there is no direct experimental evidence for it. The corrosion rate of silica glass was measured as a function of hydrostatic pressure and was found to increase with increasing pressure. This observation appears inconsistent with the stress corrosion mechanism. (Appendix C).
4. When abraded glass is soaked in water its strength increases with the soaking time. This phenomenon is usually explained in terms of

the crack blunting by the uniform dissolution of the crack tip. When the glass is soaked in water containing silicic acid which is the dissolution product of silica glass in water, the strength was found to increase faster in spite of the fact that the dissolution rate of the glass in the silicic acid-containing water is slower. It was suggested that the dissolution and precipitation rather than simple dissolution is involved in the crack blunting process. (Appendix D)

5. Fatigue characteristic of brittle material can also be determined by measuring the mechanical strength as a function of stress rate. This measurement was performed for high silica glass with various different surface conditions. It was found that glass treated with Grignard reagent or  $(\text{CH}_3)_3\text{SiCl}$  showed an extremely small fatigue tendency.

(Appendix E)



### III. PERSONNEL

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### IV. PUBLICATIONS

- 1) "Glass Surface Cracks Caused by Alkaline Solution Containing an Alkaline Earth Element", M. Tomozawa, Y. Oka and J.M. Wahl, J. Am. Ceram. Soc., 64 [2] C-32(1981) (Appendix A)
- 2) "Effect of Surface Energy on the Mechanical Strength of a High-Silica Glass", Y. Oka, J.M. Wahl and M. Tomozawa, J. Am. Ceram. Soc., 64 [8] 456 (1981) (Appendix B).
- 3) "Stress Corrosion of Silica Glass", S. Ito and M. Tomozawa, J. Am. Ceram. Soc., 64 [11] C-160 (1981) (Appendix C).
- 4) "Crack Blunting of High Silica Glass", J. Am. Ceram. Soc., to appear in August (1982) issue. (Appendix D).
- 5) "Effects of Surface Conditions on Stress-Rate Dependence of Mechanical Strength of High Silica Glass", S. Ito and M. Tomozawa. to appear in the Proceedings of the International Symposium on Fracture Mechanics of Ceramics. (1982) (Appendix E)

### V. ORAL PRESENTATION

- 1) "Stress Corrosion of High Silica Glass", S. Ito and M. Tomozawa 83rd Annual Meeting of the American Ceramic Society, Washington, D.C., May 1981.
- 2) "Surface Energy Effect on Strength of Glass", M. Tomozawa, NBS Symposium on Stress Corrosion, Washington, D.C., June 1982
- 3) "Effect of Surface Conditions on Stress-Rate Dependence of Mechanical Strength of High Silica Glass", S. Ito and M. Tomozawa International Symposium on Fracture Mechanics of Ceramics, June 1981.
- 4) "Surface Energy and Mechanical Strength of Glass", M. Tomozawa, Gordon Conference on Glass, Plymouth College, N.H., Aug. 1981.
- 5) "Microstructure of Glass Surface Reacted with Water", M. Tomozawa and S. Capella, 1981 Glass Division Fall Meeting, The American Ceramic Society, Oct. 1981.

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**APPENDIX A**



# Glass Surface Cracks Caused by Alkaline Solution Containing an Alkaline-Earth Element

M. TOMOZAWA,\* Y. OKA,\*\* AND J. M. WAHI\*

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When glass was treated in a hot alkaline solution containing a small amount of heavy alkaline earth elements such as Ba or Sr, sharp cracks formed on the glass surface. The severity of the crack formation was greater, the heavier the alkaline earth element. The cracks caused a drastic reduction in the mechanical strength of the glass.

ALKALINE solution such as NaOH dissolves oxide glasses<sup>1</sup> uniformly, leaving a clear, smooth surface. When the alkaline solution contains a minor concentration of various ions, this dissolution rate is usually retarded.<sup>2-4</sup> In the course of the investigation of this inhibitor effect, an unusual phenomenon was discovered. Namely, when certain glasses are held in alkaline solutions containing ions of the heavy alkaline earth elements, Ba or Sr, minute cracks appear on the glass surface. This is shown in Fig. 1, where SiO<sub>2</sub> microscope slide glasses<sup>5</sup> treated in 1N NaOH solution with and without 0.001 mol/L addition of BaCl<sub>2</sub> at 80°C, for 14 h are compared. When the solution contained no BaCl<sub>2</sub>, the glass surface remained clear, while BaCl<sub>2</sub>-containing solution produced numerous visible cracks. The size and number of these cracks were observed to increase with the treatment time. Prior abrasion of the specimen promoted the crack formation as can be seen in Fig. 1. A similar phenomenon was observed in Sr-containing solution also, although the severity of surface damage was less in Sr-containing solution than in Ba-containing solution. An example is shown in Fig. 2, where 96% silica glass rods<sup>6</sup> treated in both solutions are compared. No visible crack was formed on glasses treated in alkaline solution containing Be, Mg, or Ca. Thus, it appears in general that the surface crack formation tendency is greater, the larger the atomic weight of alkaline earth element in solution.

These minute cracks had, as expected, a drastic effect on the mechanical strength of glass specimens. The mechanical strength was measured using 96% silica glass rods (3 mm in diam., 6.4 cm long) at room temperature and in air (rh 50%) using a four-point

bending method. In Fig. 3, the mechanical strength, at a constant stress rate of  $1.7 \times 10^2$  MPa/min, of the glass rods treated in 1N NaOH, 1N NaOH + 0.001 mol/L SrCl<sub>2</sub>, or

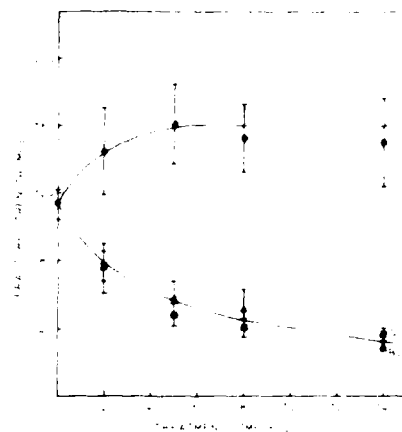


Fig. 3. Mechanical strength of 96% SiO<sub>2</sub> glass rods as a function of solution treatment time. Each data point represents the average for 30 specimens; bar represents  $\pm$  standard deviation. (○) 1N NaOH, (■) 1N NaOH + 0.001 mol/L SrCl<sub>2</sub> solution, and (▲) 1N NaOH + 0.001 mol/L BaCl<sub>2</sub> solution. Data were obtained at room temperature in air (rh = 50%).

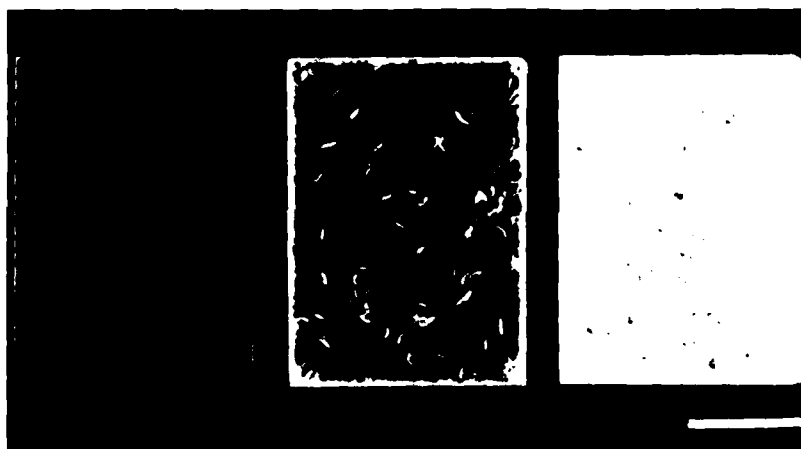


Fig. 1. Surface condition of SiO<sub>2</sub> slide glass after immersion in (left) 1N NaOH and (center) 1N NaOH + 0.001 mol/L BaCl<sub>2</sub> solution for 14 h at 80°C. Sample on right was abraded with 600-grit SiC paper before it was immersed in 1N NaOH + 0.001 mol/L BaCl<sub>2</sub> solution (bar = 1 cm).



Fig. 2. Surface condition of 96% SiO<sub>2</sub> glass rod after immersion in (left) 1N NaOH, (center) 1N NaOH + 0.001 mol/L SrCl<sub>2</sub> solution, and (right) 1N NaOH + 0.001 mol/L BaCl<sub>2</sub> solution at 80°C for 14 h (bar = 1 cm).

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1N NaOH + 0.001 mol/L BaCl<sub>2</sub> is shown as a function of the treatment time at 80°C. It can be seen from the figure that the drastic decrease in strength occurs in <2 h when the glass is treated with alkaline solution containing Sr or Ba, while no such strength degradation takes place for glasses treated with 1N NaOH solution. The strength of glasses treated in Ba- or Sr-containing solutions keeps decreasing with time, reaching as low as  $\approx 1/5$  of its strength for the specimen treated in Ba- or Sr-free solution in 14 h. It is known that when alkali metal ions are contained as a glass component, they can exchange with other ions from an external source. This ion exchange can produce compressive<sup>5</sup> or tensile stresses<sup>6</sup> depending upon the relative size of the exchanging ions. In the present experiment, however, this type of ion exchange is unlikely since the alkali content in the glass specimens used is extremely low.

Alkaline earth elements were found<sup>1</sup> to deposit on the glass surface and reduce the alkaline attack while other ions such as Zn and Al were not. It is most likely that heavy alkaline earth ions deposit in the preexisting microcracks and cause a crack extension. This phenomenon can be utilized as a means to observe surface flaws.

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**APPENDIX B**

# Effect of Surface Energy on the Mechanical Strength of a High-Silica Glass

Y. OKA\*\* J. M. WAHL,\* and M. TOMOZAWA\*

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The mechanical strength of high-silica glass was measured in various organic liquids and in water. The extent of the surface-energy reduction of glass was also estimated from the swelling or the expansion of porous glass, immersed in liquids, by measuring the stress in the core of a partially leached glass. The stress, normalized to the value in water, showed a good correlation with the heat of immersion, which is a measure of the surface-energy reduction. Mechanical strength and the stress due to swelling showed a reasonable correlation, suggesting that the strength variation in various liquids is due to the surface-energy variation and the accompanying force which caused the swelling.

## I. Introduction

THE mechanical strength of glass is strongly influenced by the environment in which it is measured. For example, the fracture strength measured in water is approximately one-half of that in vacuum.<sup>1,2</sup> Similar strength reduction was observed in organic solvents.<sup>1-5</sup> There are several suggested mechanisms for the phenomenon. Charles and Hillig explain it in terms of chemical attack at the crack tip by water.<sup>6</sup> The reduction in strength in an inert environment, such as organic solvents, could be attributed to the residual water in the organic solvent. To test this mechanism, therefore, organic solvents free of trace amounts of water must be used. Another mechanism was suggested by Orowan,<sup>7</sup> who attempted to explain the lower strength of glass in water in terms of the lower surface energy. It is known that the surface energy of glass is reduced when the specimen is immersed in water. To relate this lowering of the surface energy to the mechanical strength, Orowan used the Griffith equation,<sup>8</sup> which expresses the mechanical strength as a function of the surface energy. Subsequently, several investigators<sup>1,5,9</sup> used this mechanism to explain the strength reduction of glass in organic solvents as well as in water vapor. The surface energy in the Griffith equation, however, is the fracture surface energy<sup>9</sup> and, although it may be broadly interpreted, as was done by Orowan, to include the effect of the test environment, its relation to the ordinary surface energy which can be evaluated nondestructively<sup>10-12</sup> is not clear. Earlier it was shown<sup>13</sup> by the present authors that the mechanical strength variation in various environments is related to the reduction of the surface energy of glass and the swelling by using a characteristic of liquid called polarity. Here it will be shown that essentially the same conclusion can be reached by using a more popular concept, i.e. heat of immersion,<sup>14</sup> which is a direct measure of the surface-energy reduction of a solid immersed in a liquid.

## II. Experimental Procedure

### (1) Mechanical Strength Measurement

Commercial 96% fused silica glass rods<sup>†</sup> were used to measure mechanical strength by the four-point bending method. The glass rods (3 mm in diam.) were cut into approximately 6.4 cm lengths and dried at 150°C for 3 h. The drying temperature of 150°C was chosen since physically adsorbed water is known<sup>15</sup> to be eliminated by heating at this temperature for a short time. The glass surface

was abraded by putting 30 glass rods in a 2 L jar mill with 70 g of 0.3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  dry powder in vacuum and tumbling them for 30 min.  $\text{Al}_2\text{O}_3$  powder was heated in vacuum at 400°C for 6 h to remove water in the powder immediately before placement in the jar mill. Vacuum in the container during drying as well as in the jar mill was  $<1.3$  Pa. After abrasion, the glass rods were washed in an ultrasonic cleaner in the same organic solvent as that to be used in the mechanical-strength measurement. The fracture strength was measured after immersing a specimen for at least 30 min in water or in organic solvents dried by molecular sieves<sup>†</sup> in advance of the test. Preliminary investigation on the stress-rate dependency indicated that, although the mechanical strength of glass varies with the stress rate, its stress-rate dependency is similar in both water and an organic solvent. This suggests that the relative strength in various liquids is independent of stress rate. Consequently, all the subsequent measurements were conducted at a constant stress rate of  $1.7 \times 10^2$  MPa/min.

### (2) Surface-Energy Measurement by Swelling

There is no accurate, direct method to measure the surface energy of glass rods in liquids. When a glass specimen with a large surface area is available, the heat of immersion, which is a measure of the reduction of the surface energy, can be determined. Another method is to use the phenomenon of swelling. That is, when a solid material with a large surface area is immersed in a liquid, the volume of the solid specimen increases and the amount of the volume increase is proportional to the reduction of the surface energy. The volume change can be measured directly. But here, for better accuracy,<sup>16</sup> the extent of swelling, or the volume increase of glass in various liquid environments, was determined by measuring the stress built up in a glass layer between two expanding layers. It was anticipated that this swelling phenomenon can bridge two apparently unrelated effects, viz. the surface-energy effect and the mechanical effect.

The glass sample used in the swelling study was a borosilicate glass rod<sup>‡</sup> with the nominal composition of  $\text{SiO}_2$  70,  $\text{B}_2\text{O}_3$  23,  $\text{Na}_2\text{O}$  7 wt%.

The borosilicate glass rod (6 mm in diam.) was heat-treated at 550°C for 3 days to induce phase separation. The phase-separated rod was cut (2.5 by 3 mm in cross section by 100 mm long) and immersed in 3N HCl saturated with  $\text{NH}_4\text{Cl}$  at room temperature to leach out the alkali borate-rich phase. Leaching was stopped at approximately half-way and the partially leached bar was cut into pieces 3 mm long. A glass piece was rinsed in water and then dried in an oven at 400°C for 5 h to remove any organic residue. The specimen was immediately placed in water or organic solvent which was dried with molecular sieves, and the stress in the center of the unleached core produced by swelling of the leached clad was measured at room temperature using a polariscope.<sup>†</sup>

A micrometer-slide cathetometer with telemicroscope\*\* was used to observe the birefringence in the specimen placed in the polariscope. The analyzer of the polariscope was rotated with respect to the polarizer and the quarter-wave plate until the minimum light transmission through the specimen was observed and the birefringence in the specimen was estimated from the amount of the analyzer rotation. The accuracy of the measurement was  $\pm 2^\circ$  in the analyzer rotation angle, which corresponded to  $\pm 2$  to  $\approx 3$  nm/mm of birefringence in the present experimental arrangement. The stress in the unleached core, rather than in the leached clad, was

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‡No. 7900, Corning Glass Works, Corning, N.Y.

†Type 3A, Linde Div., Union Carbide Corp., Morristown, N.J.

‡Custom-made glass, Owens-Illinois Technical Center, Toledo, Ohio.

†Model No. 204, Polarizing Instrument Co., Inc., Peekskill, N.Y.

\*\*Gaertner Scientific Corp., Chicago, Ill.

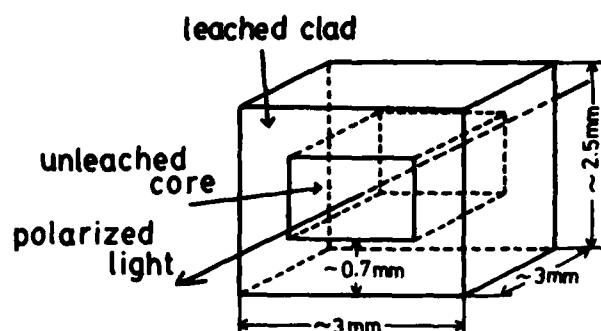


Fig. 1. Partially leached glass specimen and polarized light path for stress measurement with a polariscope.

Table 1. Fracture Strength of High-Silica Glass Rods\* in Organic Solvents

Liquid	Fracture strength ( $10^2$ MPa) <sup>†</sup>
CCl <sub>4</sub>	$1.48 \pm 0.18$
Aniline	$1.37 \pm 0.19$
Benzene	$1.36 \pm 0.18$
CHCl <sub>3</sub>	$1.28 \pm 0.12$
Ethanol	$1.28 \pm 0.19$
Formamide	$1.23 \pm 0.10$
Nitrobenzene	$1.14 \pm 0.14$
Methanol	$1.07 \pm 0.12$
Water	$1.05 \pm 0.17$

\*Vycor, Corning 7900, Corning Glass Works, Corning, N.Y. <sup>†</sup>Stress rate  $1.7 \times 10^2$  MPa/min.

measured to avoid the effect of possible microstructural birefringence of porous glass.<sup>17</sup> Orientation of the specimen with respect to the polarized light path is indicated in Fig. 1. Because of the rectangular cross section, the strains in two directions perpendicular to the light-path direction are different in magnitude and a birefringence appears. The magnitude of the birefringence is proportional to the stress, which in turn is proportional to the amount of expansion of the clad. Thus, although the absolute magnitude of the stress or the expansion cannot be determined by this measurement, the relative magnitude can be determined accurately.

The amount of swelling of the leached layer and the consequent stress generated in the unleached layer are strongly influenced by the surface area and the surface condition of the specimen. Therefore, it is important to use the same specimen with the same surface condition for various liquids to compare the effects of different liquids. Thus, the following procedure was used. The specimen was dried at 400°C for 5 h for cleaning and then immersed in water to measure stress due to swelling. Subsequently, the specimen was dried at 400° or 80°C for 5 h and immersed in each liquid. The birefringence was found to increase with immersion time, reaching a steady-state value in 12 h. This steady-state value was designated as  $S$ . These values of  $S$  in various liquids were normalized to the value in water,  $S_0$ , for the same sample in water after 12 h. Namely, the process can be expressed as follows:

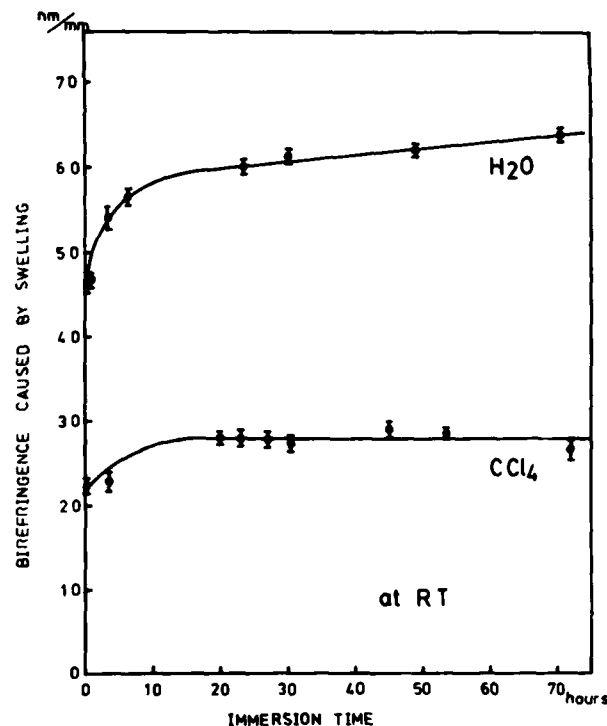
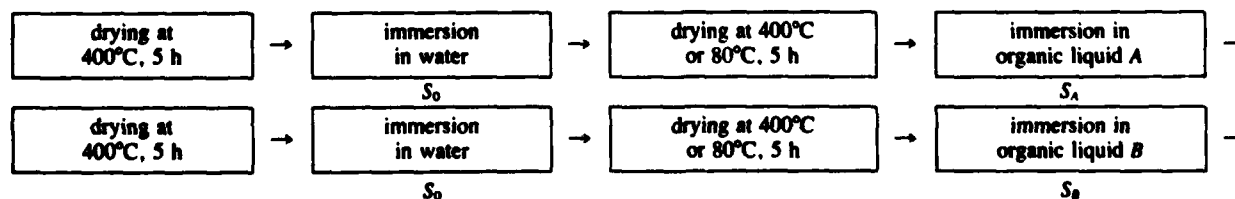


Fig. 2. Immersion time dependence of birefringence in unleached core in water and CCl<sub>4</sub>; birefringence is expressed by optical retardation. The specimen was dried at 400°C for 5 h before immersion.

When the glass used for the swelling experiment is heat-treated for phase separation, and completely leached and subsequently heated for consolidation, it turns into a glass<sup>18</sup> similar to the high-silica glass used in the mechanical strength measurement of the present experiment. Thus the phase-separated and leached clad has a composition identical to that of the commercial high-silica glass.<sup>1</sup> Therefore, the mechanical-strength data can be directly compared with the swelling data, since both refer to the same glass composition.

### III. Results

#### (1) Mechanical Strength

The mechanical strength of glass in various liquids is shown in Table I in descending order. Here 30 data points were averaged for each liquid and the error range indicates  $\pm$  standard deviation. It can be seen that the strength varies widely from the highest value of  $(1.48 \pm 0.18) \times 10^2$  MPa in CCl<sub>4</sub> to the lowest value of  $(1.05 \pm 0.17) \times 10^2$  MPa in water.

#### (2) Surface-Energy Measurement by Swelling

When a leached specimen was immersed in liquid, the specimen expanded slowly since a liquid penetrates slowly into the smallest pores, replacing air. Corresponding to the swelling of the leached clad, the stress and the birefringence in the unleached core increased with the immersion time, reaching a steady state value in approximately 12 h, as shown in Fig. 2 for CCl<sub>4</sub>. Water was

Table II. Normalized Swelling Stresses in Organic Solvents

Liquid	$S/S_0$ *	
	Dried at 400°C	Dried at 80°C
CS <sub>2</sub>	0.22 ± 0.01	0.52 ± 0.02
Benzene	.22 ± 0.02	.57 ± 0.03
CCl <sub>4</sub>	.23 ± 0.03	.55 ± 0.03
Toluene	.23 ± 0.02	.55 ± 0.02
Nitrobenzene	.24 ± 0.02	.60 ± 0.05
Chlorobenzene	.24 ± 0.04	.57 ± 0.02
CHCl <sub>3</sub>	.25 ± 0.02	.65 ± 0.06
Aniline	.30 ± 0.03	.62 ± 0.05
Pyridine	.31 ± 0.01	.71 ± 0.03
Ethanol	.37 ± 0.02	.71 ± 0.02
Propanol	.42 ± 0.02	.70 ± 0.03
Formamide	.49 ± 0.02	.75 ± 0.03
Methanol	.51 ± 0.02	.87 ± 0.03

\*Specimens were dried for 5 h at temperature indicated before they were immersed in organic solvents.  $S$  and  $S_0$  are the stresses in the unleached core in the organic solvent and water, respectively.

somewhat exceptional and the birefringence kept increasing, as shown in the same figure. The birefringence, which is proportional to the stress generated by swelling, expressed by a normalized form  $S/S_0$  obtained after 12-h immersion in liquid, is shown in Table II for both 400° and 80°C drying. The reproducibility was checked by repeated measurement of  $S_0$  and was found to be satisfactory. The results show that the lowest normalized stress is observed in solvents such as CS<sub>2</sub>, benzene, and CCl<sub>4</sub>, whereas the largest stress was generated in water.

#### IV. Discussion

Swelling, the volume expansion, of glass can take place by various mechanisms, one of which is the chemical reaction or ion exchange observed in electrode glass.<sup>19</sup> In the present experiment, alkali content in glass specimens was too low to observe this type of phenomenon; the swelling observed in the porous glass was related to the surface-energy reduction.

Yates<sup>12</sup> showed that the following equation is applicable to the expansion of the porous glass by gas adsorption:

$$\Delta l/l = (2\Sigma\rho/9K)\Delta\gamma \quad (1)$$

where  $l$  and  $\Delta l$  are the original length and length change of the specimen, respectively,  $\Sigma$  is the specific surface area;  $K$  the bulk modulus,  $\Delta\gamma$  the surface-energy reduction, and  $\rho$  the density of the glass portion of the porous glass. This expression has been confirmed experimentally.<sup>20,21</sup> In the present experiment, when a porous clad expanded by reduction of the surface energy, a corresponding stress increase was observed in the core. Since the stress in the unleached core, which existed before the swelling took place, is much smaller than the observed stress,  $S/S_0$  is considered to be approximately proportional to the reduction of the surface energy. This conclusion can be further confirmed by comparing the stress caused by swelling with the heat of immersion, which is identified with the reduction of the surface energy in liquid. Comparison is made in Fig. 3 for selected liquids. Although the data for heat of immersion for SiO<sub>2</sub> (which has a similar composition to the glass used in this investigation) are limited, according to Boyd and Harkins<sup>22</sup> the heat of immersion normalized to that in water,  $h_i/h_{i,H_2O}$ , depends almost entirely on the nature of the liquid and not on the type of oxide immersed. Thus, in this figure both values for TiO<sub>2</sub> and SiO<sub>2</sub> are used. Figure 3 shows a good correlation between the swelling stress and the heat of immersion, both normalized to values in water. This result indicates that the swelling measured here is a good indication of the surface-energy reduction of glass.

The relation between the mechanical strength in various solvents and the observed  $S/S_0$  values are shown in Figs. 4(A) and 4(B). A reasonable correlation between the strength and  $S/S_0$  is observed, with the only exception being nitrobenzene, which is known to be

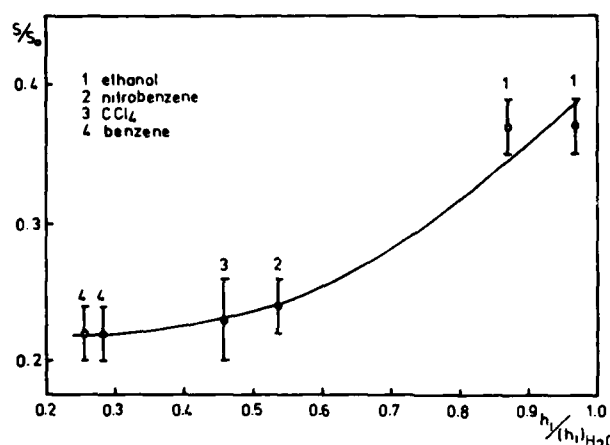


Fig. 3. Relation between stress in core of partially leached glass immersed in various liquids normalized to the value in water vs normalized heat of immersion. (●) TiO<sub>2</sub>, (○) SiO<sub>2</sub> (Ref. 22).

unique. For example, other investigators<sup>1</sup> observed lower mechanical strength in this liquid than in water. Also, according to Kuznetsov,<sup>23</sup> most liquids show a good correlation between their dielectric constant and the surface energy of glass in the liquid, whereas nitrobenzene deviates from the trend, showing a greater surface energy of glass than expected. (A small amount of acid (HNO<sub>3</sub>) in the solvent may be responsible for the deviation.) Because of the anomaly of this liquid, although the exact reason for it is not known, the data point for this liquid is shown using a different symbol in Figs. 4(A) and 4(B). With these considerations, it can be seen that there is a reasonable correlation between the mechanical strength and the extent of swelling, which is a measure of the surface-energy reduction.

The slight difference between Figs. 4(A) and 4(B) can be attributed to the different surface conditions of the glass produced by different drying temperatures. It is well known<sup>24,25</sup> that the surface hydroxyl concentration decreases with increasing drying temperatures and that water<sup>15</sup> as well as organic solvents such as benzene<sup>25</sup> and methyl alcohol<sup>26</sup> are adsorbed on the surface hydroxyl. Thus, the surface hydroxyl concentration and the amount of swelling in a given solvent of a specimen dried at 400°C are expected to be less than those of a specimen dried at 80°C.

These observations clearly establish that the mechanical strength correlates well with the surface-energy reduction. As was pointed out, Orowan's mechanism<sup>7</sup> is not satisfactory since the relation between the surface energy and the fracture surface energy in the Griffith equation is not clearly established. The real function of the surface energy in the mechanical strength, therefore, is not explicitly included in the Griffith equation. Here, it is suggested that a mechanical force due to the surface energy which produced swelling is responsible for the observed strength variation. That is, when the surface energy is reduced the corresponding mechanical force changes, causing swelling of the surface layer. It is speculated that this mechanical force due to the surface energy changes the mechanical strength of glass either directly by changing the local stress and the elastic energy or indirectly by changing the crack-tip radius.<sup>27</sup> For example, the surface energy produces a pressure which is proportional to the surface energy and reciprocally proportional to the radius of curvature. Thus this pressure is expected to be large at the crack tip and it works to increase the radius of curvature at the crack tip. When a glass specimen is immersed in water and the surface energy is reduced, this pressure is reduced and the radius of curvature at the crack tip is expected to become smaller. This would lead to the greater stress concentration at the crack tip and the lower mechanical strength in water.

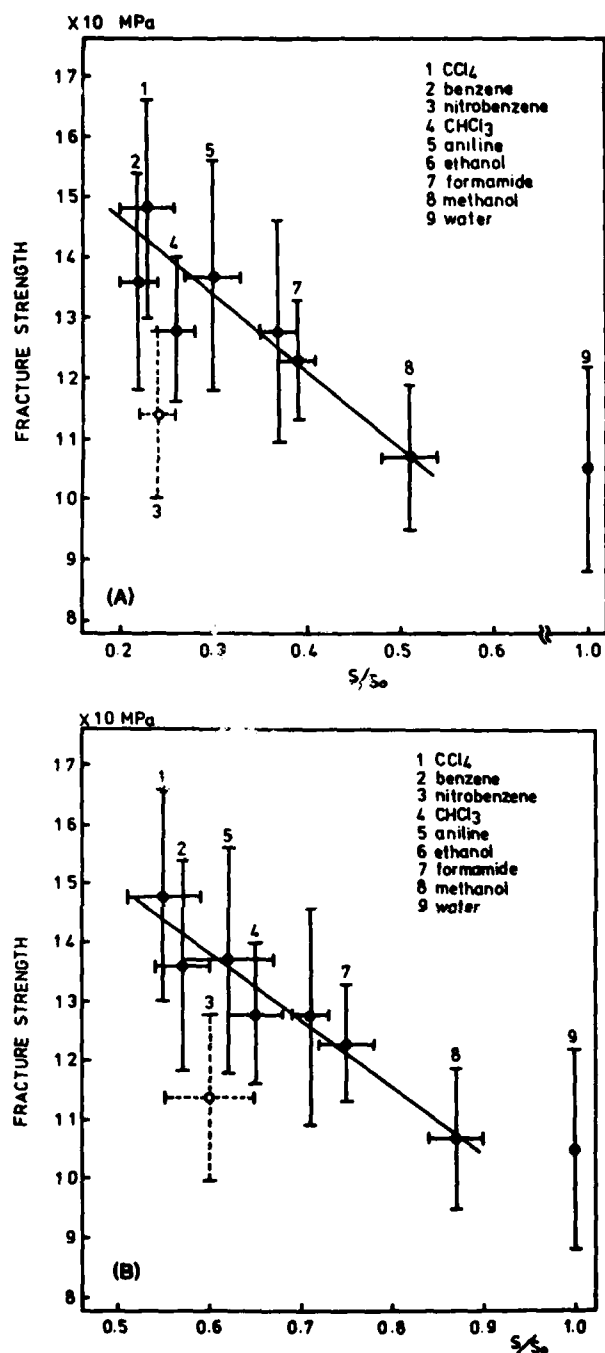


Fig. 4. Fracture strength of high-silica glass rods vs normalized swelling stress ( $S/S_0$ ) in organic solvents (stress rate  $1.7 \times 10^3$  MPa/min) for specimens dried for 5 h at (A) 400° and (B) 80°C before swelling stress measurement.

### (1) Effect of Residual Water

It is important to consider the possible effect, on the present observations, of impurity water in various organic solvents since water has the greatest effect on both mechanical strength and swelling of glasses. In the present experiment, reagent-grade chemicals were used and all liquids were treated with a molecular sieve. The specified concentrations of water in these organic solvents before treatment with the molecular sieve are shown, together with the solubility<sup>28</sup> of water in selected organic solvents, in Table III. It has been claimed<sup>29</sup> that, after molecular sieve treatment, the water

Table III. Solubility and Specified Water Content of Organic Solvents Before Molecular Sieve Treatment

Liquid	Specified conc. (wt%)	Solubility at 25°C (wt%)
CCl <sub>4</sub>	0.01	0.01
CS <sub>2</sub>	<0.05	.01
Toluene	0.01	.05
Benzene	0.05	.06
Chlorobenzene	0.02	.04
CHCl <sub>3</sub>	(0.75 C <sub>2</sub> H <sub>5</sub> OH)	.08
Pyridine	0.05	
Nitrobenzene	(0.003 HNO <sub>3</sub> )	
Aniline		
Propanol		
Ethanol	(Anhydrous)	
Methanol	0.05	
Formamide		

content is reduced to <10 ppm in most cases and to <1 ppm in some cases.

When a dried glass is placed in such solvents, water will be adsorbed on the glass surface selectively.<sup>30-32</sup> The fugacity,  $f$ , of water in a solvent with extremely low concentration,  $X$ , of water is given<sup>30</sup> approximately by

$$f = P_0 (X / X^s) \quad (2)$$

where  $P_0$  is the saturation vapor pressure of the pure water and  $X^s$  is the solubility of water in the solvent. If we take benzene containing 1 ppm of water at 25°C as an example of solvent,

$$f = 3.17 \text{ MPa} \times [10^{-6} / (0.06 \times 10^{-2})] = 0.00528 \text{ MPa} \quad (3)$$

It is possible, using this fugacity value, to estimate the extent of the selective water adsorption from the solvent on the glass surface.<sup>31,32</sup> The maximum amount of water adsorption can be obtained by assuming that the solvent is not adsorbed and using the adsorption data of pure water vapor with the same vapor pressure.<sup>31</sup>

From the adsorption isotherm, the reduction,  $\pi$ , of the surface energy of the solid can be calculated,<sup>11</sup> using the following equation:

$$\pi = RT / V \sum \int_0^P (v / P) dP \quad (4)$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $V$  the molar volume of gas,  $\sum$  the specific surface area of the solid,  $P$  the equilibrium pressure of the adsorbed gas, and  $v$  the volume of gas adsorbed per gram of solid. Using this relation, Boyd and Livingston<sup>33</sup> estimated the surface-energy reduction of SiO<sub>2</sub> on immersion in saturated vapor at 25°C and obtained  $244 \times 10^{-7}$  J/cm<sup>2</sup> for water and  $52 \times 10^{-7}$  J/cm<sup>2</sup> for benzene. The reduction in the surface energy of the specimen immersed in the corresponding liquids is expected to be larger. The reduction in the surface energy of a solid can be obtained as a function of vapor pressure using the same equation.

When porous high-silica glass is immersed in benzene containing 1 ppm of water, the reduction in the surface energy of the solid is estimated, by assuming that benzene is not adsorbed on the glass surface, to be <1.5% of the surface-energy reduction in the saturated water vapor.<sup>34</sup> If the values obtained by Boyd and Livingston<sup>33</sup> are used here, the surface-energy reduction due to 1 ppm impurity water in benzene is  $<3.7 \times 10^{-7}$  J/cm<sup>2</sup>, far smaller than the surface-energy reduction by pure benzene,  $52 \times 10^{-7}$  J/cm<sup>2</sup>. This difference is actually even greater, since the amount of water adsorption from benzene containing 1 ppm water is less, whereas the surface-energy reduction by pure benzene liquid is larger than the above value obtained for the saturated benzene vapor. Thus, the effect of a trace amount of water can be neglected here.

It is known that a small amount of water vapor in air or N<sub>2</sub> gas<sup>35</sup> can influence the mechanical strength and a similar effect may be expected for the measurement in organic solvents. From the above discussion, however, it is clear that there is a subtle difference, as far as the effect of a small amount of water is concerned, between

the measurement in air (or  $N_2$  gas) and that in organic solvents.<sup>30</sup> In the case of the measurement in air (or  $N_2$  gas) at room temperature, only water vapor can be adsorbed and other species such as  $O_2$  or  $N_2$  can hardly be adsorbed. Therefore, a small amount of water vapor can have a damaging effect on the mechanical strength. On the other hand, in the measurement in organic solvent, in addition to the selective adsorption of impurity water on the glass surface, the solvent itself, which is the major component, such as benzene, can also be adsorbed. And, as long as the effect of the adsorbed organic solvent outweighs the effect of the adsorbed water, the effect of water on the measurement can be neglected.

### V. Conclusions

A correlation was found between the mechanical strength of a high-silica glass in various liquids and the extent of swelling or the expansion of the specimen, determined by the stress measurement in the unleached core of the partially leached porous borosilicate glass. The swelling is a measure of reduction of the surface energy. It was suggested, therefore, that the strength variation of glass in liquid can be explained by the change in mechanical force due to the surface energy, which caused the swelling.

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**APPENDIX C**

# Stress Corrosion of Silica Glass

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*Dissolution rate of silica glass in water was measured as a function of hydrostatic pressure at 285°C and was found to increase with increasing pressure. This observation appears to be contrary to the stress-corrosion hypothesis of the static fatigue of glass.*

**F**ATIGUE phenomena of glass are often explained by a stress-corrosion mechanism originally developed by Hillig and Charles.<sup>1</sup> According to this mechanism, the reaction of glass with water (corrosion) is accelerated by tensile stress and the reaction rate (corrosion rate)  $v$ , is given by:

$$v = v_0 \exp \left( -\frac{V^* \sigma}{RT} \right) \quad (1)$$

where  $v_0$  is the reaction rate under zero stress,  $\sigma$  the stress, being negative for tensile stress,  $V^*$  the activation volume which is assumed positive,<sup>1,2</sup> and  $R$  and  $T$  have their usual meaning. This accelerated reaction produces either a crack extension or a sharpening of the crack tip, which increases the stress concentration at the crack tip,<sup>3</sup> eventually leading to the mechanical failure of the glass.

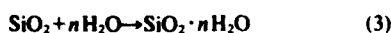
However, there is no direct experimental evidence of the stress-accelerated corrosion of silica glass. It is true that the experimental observation of the fatigue phenomenon can be explained by the model reasonably well and the crack extension measurement appears to support Eq. (1),<sup>4</sup> but there is no proof that the crack extension rate is equal to the glass corrosion rate.

In general, there can be many types of corrosion reaction of glass by water, including water-alkali ion exchange. But here, only  $\text{SiO}_2$  glass is considered and

reaction such as water-alkali ion exchange is excluded. The reaction considered by Hillig and Charles is:



If this reaction is continued, the dissolution of glass into water takes place by:



where  $n$  is an integer and the value is usually taken as two.<sup>5</sup> To modify the crack geometry by corrosion, this dissolution equation is considered necessary; Hillig and Charles discuss the flaw geometry change due to corrosion or dissolution.

According to the chemical reaction rate theory,<sup>6</sup> if in the reaction (3), the reactants go through an activated complex which has a unique volume, to the resulting product, the following equation can be obtained for the reaction rate constant,  $k$ :

$$\frac{\partial \ln k}{\partial P} = -\frac{\Delta V^*}{RT} \quad (4)$$

where the activation volume  $\Delta V^*$  is the partial molar volume of the activated complex minus that of the reactants. If  $\Delta V^*$  is independent of pressure:

$$k = k_0 \exp \left( -\frac{\Delta V^* P}{RT} \right) \quad (5)$$

where  $k_0$  is the rate constant in the absence of external pressure. This relation has been found to hold for many reactions with  $\Delta V^*$  ranging from  $-50$  to  $+20 \text{ cm}^3/\text{mol}$ .<sup>7</sup>

Equation (1) is similar to Eq. (5), but in Eq. (5),  $P$  is the hydrostatic pressure while in Eq. (1),  $\sigma$  is the uniaxial stress. In this work, Eq. (5) was evaluated to learn the validity of Eq. (1).

The dissolution rate of silica glass ( $\approx 3 \text{ mm}$  in diam. and  $3 \text{ cm}$  in length) in water at  $285^\circ\text{C}$  was measured as a function of hydrostatic pressure using a hydrothermal high-pressure unit. The sample glass rod and distilled water were placed in a high-pressure stainless steel tube and various pressures up to  $247 \text{ MPa}$  ( $2520 \text{ kg/cm}^2$ ) were applied by water as a pressurizing medium. Then the tube was placed in a furnace kept at  $285^\circ\text{C}$ . After treatment, the tube was pulled out from the furnace and was immersed in water to quench the sample. The reduction of the diameter of the sample rod was calculated from the weight loss, surface area, and density of the glass. The results are summarized in Figs. 1 and 2. It can be seen that the general form of Eq. (5) is satisfied in this case. However, the activation volume is found to be  $-27 \text{ cm}^3/\text{mol}$ , a negative quantity, contrary to the assumption used in Eq. (1). In the present measurement under hydrostatic pressure, both glass specimen and water are pressurized uniformly, while in the mechanical strength measurement, only the glass specimen is stressed. Therefore the possible effect of this difference on the activation volume should be considered. Activation volume  $\Delta V^*$  of reaction (3) can be expressed, from the reaction rate theory, as:

$$V^* = V_{\text{act}} - V_{\text{SiO}_2} - nV_{\text{H}_2\text{O}} \quad (6)$$

where  $V_{\text{act}}$  is the volume of the activated complex, and  $V_{\text{SiO}_2}$  and  $V_{\text{H}_2\text{O}}$  are the volumes of  $\text{SiO}_2$  glass and water, respectively.  $\Delta V^*$  was found, by the present experiment, to be negative under hydrostatic pressure. If only glass is subjected to the stress, the volume of water  $V_{\text{H}_2\text{O}}$  is expected to be larger and  $\Delta V^*$  should be more negative than what is found here. Thus the present observation casts a doubt on the stress corrosion mechanism of fatigue phenomena of glass, which is based on Eq. (1) with positive activation volume.

It is possible, although not probable, that the dissolution rate of  $\text{SiO}_2$  glass increases both with tensile and compressive stress. Also, a stress gradient near the crack tip may accelerate the corrosion reaction. These possibilities have to be explored before the stress-corrosion mechanism is completely abandoned.

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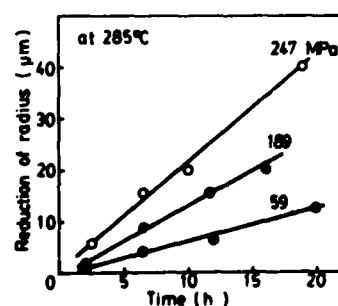


Fig. 1. Reduction of radius as a function of time for silica glass rod held under pressure, at  $285^\circ\text{C}$ .

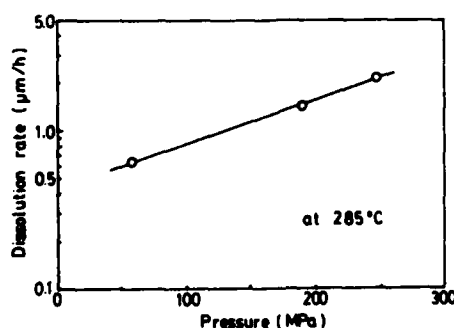


Fig. 2. Dissolution rate of silica glass as a function of pressure at  $285^\circ\text{C}$ .

**APPENDIX D**

## Crack Blunting of High-Silica Glass

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The mechanical strength of abraded high-silica glass was measured after immersion in water and silicic acid solution at room temperature and 88°C. The strength increase was observed at 88°C. This phenomenon is usually explained by crack blunting. From an observation of the dissolution rate of a porous glass with a similar composition and a comparison of the strength increase in water and silicic acid, it was concluded that the dissolution and subsequent precipitation of the high-silica glass is the mechanism of the crack blunting.

### I. Introduction

THE strength of an abraded glass rod increases when the rod is held in water. This phenomenon is usually explained by the blunting of the crack tip.<sup>1</sup> It is believed that the radius of curvature of the crack tip becomes larger due to a chemical reaction of the glass with water, causing the stress concentration at the crack tip at the time of loading to decrease and the strength to increase. However, the details of the phenomenon and the mechanism of the crack blunting are not clear.

In the present work, the effect on mechanical strength of soaking high-silica glass in H<sub>2</sub>O and in an Si(OH)<sub>4</sub> solution was investigated and compared with the chemical corrosion rate of the glass, to clarify the mechanism of the crack blunting. The high-silica glass, rather than alkali-containing glasses, was used to avoid the possible complication due to alkali-water ion exchange which can produce the surface stress.<sup>2</sup>

### II. Experimental Procedure

Commercial high-silica glass rods (≈3 mm in diam.) were used for the strength measurement. This glass contains only 0.02 wt% Na<sub>2</sub>O and 0.02 wt% K<sub>2</sub>O, and the effect of ion exchange is considered to be minimal. The glass rods were cut into ≈6-cm lengths and the surface of the glass was abraded by tumbling the rods in a 1 L jar with SiC abrasives (600 grit) for 2 h. Subsequently, the glass rods were kept in water and in the Si(OH)<sub>4</sub> aqueous solution at room temperature and at 88°C for various lengths of time. The Si(OH)<sub>4</sub> solution was prepared by suspending 2 g of finely ground silica gel in 1 L of water at room temperature and at 88°C for 10 days. The mechanical strength of the glass rods was measured in H<sub>2</sub>O or in the Si(OH)<sub>4</sub> solution at room temperature by the four-point bending method. The strength of the specimen soaked in water was measured in water, whereas that of the specimens soaked in Si(OH)<sub>4</sub> solution was measured in that solution. There was no difference between the strength measured in H<sub>2</sub>O and that in the Si(OH)<sub>4</sub> solution when the same sample was used. Since the mechanical strength is known to be influenced by the stressing rate, a constant stressing rate of  $9.0 \times 10^2$  MPa·min<sup>-1</sup> was used. About 30 specimens were used to obtain one data point. For selected specimens, the mechanical strength was also measured in liquid nitrogen.

To correlate the change of the mechanical strength of the glass held in H<sub>2</sub>O and the Si(OH)<sub>4</sub> solution with the phenomena on the glass surface, the dissolution rate of glass was measured in both solutions. Since the glass rods used in the mechanical strength measurement had a low dissolution rate in these liquids for these treatment times and temperatures, a high-silica porous glass was used to study the surface phenomena. This porous glass had the same composition as the high-silica glass rods and a large surface area. It was prepared by heat-treating an alkali borosilicate glass<sup>3</sup> (7 wt% Na<sub>2</sub>O, 23 B<sub>2</sub>O<sub>3</sub>, 70 SiO<sub>2</sub>) at 550°C for 72 h to obtain phase separation and subsequently leaching the alkali borate-rich phase in 3N HCl saturated with NH<sub>4</sub>Cl at room temperature. The leached porous glasses were then heated at 400°C for 5 h. When the porous glass is heated to a high enough temperature, the high-silica glass used for the mechanical strength measurement can be produced. To determine the dissolution rate, the porous glass with a mass of ≈1 g was immersed in 0.1 L H<sub>2</sub>O and the Si(OH)<sub>4</sub> solution at room temperature and at 88°C for various lengths of time. Subsequently, the porous glass specimen was immersed in fresh distilled water at room temperature and cleaned using an ultrasonic cleaner for ≈5 min. This cleaning procedure was repeated twice, using fresh distilled water each time. Then the specimen was held in fresh distilled water for 1 h and weighed while still in the water. Because of the large surface area of the porous glass, the dissolution of an extremely thin surface layer becomes detectable by the weight loss measurement. The dry porous glass, however, adsorbs moisture which obscures the true weight change of the specimen. To avoid error due to the moisture adsorption, the weight change was followed by weighing the specimen in water at room temperature; the results were converted to the weight change in air by taking the buoyancy of the specimen in water into account. An elaborate cleaning procedure was used to remove the dissolved glass from the pores. Even if the dissolved glass is not completely removed from the pores, however, its effect on the density of water in the pores is small since the solubility of Si(OH)<sub>4</sub> in water is small (≈120 ppm at room temperature) and thus the error in the weight loss measurement is small. The surface area of the porous glass was measured by the BET method.<sup>4</sup>

The

described  
above

### III. Results

The mechanical strengths of glass rods measured in  $H_2O$  and in the  $Si(OH)_4$  aqueous solution at room temperature are shown in Fig. 1 as a function of soaking time and temperature. It is seen that the strength of the glass held in the  $Si(OH)_4$  solution at  $88^\circ C$  increases rapidly in the first  $\approx 240$  h and then remains practically unchanged, whereas the strength of specimens held in  $H_2O$  at the same temperature increases gradually with increasing soaking time and, after 360 h, the strength approaches that of specimens held in the  $Si(OH)_4$  solution at  $88^\circ C$ . The strength of glass held in  $H_2O$  and the  $Si(OH)_4$  solution for 360 h at  $88^\circ C$  is higher by  $\approx 30\%$  than that of freshly abraded glass.

The strengths of specimens corresponding to points A, B, and C in Fig. 1 were also measured in liquid  $N_2$  and their values were found to be  $134 \pm 10$ ,  $155 \pm 7$ , and  $161 \pm 9$  MPa, respectively. However, the strength of glass held in  $H_2O$  and the  $Si(OH)_4$  solution at room temperature remains practically unchanged.

The weight changes of porous high-silica glass in  $H_2O$  and the  $Si(OH)_4$  solution at  $88^\circ C$  are shown in Fig. 2. The results are shown also in terms of the thickness lost, assuming that the entire initial surface is removed uniformly, using the value of the initial surface area,  $140 \text{ m}^2/\text{g}$ , and the density of the high-silica glass,  $2.18 \text{ g/cm}^3$ . Figure 2 shows that the weight of glass held in water decreases linearly with soaking time in the first  $\approx 100$  h and then more slowly, and that the weight loss of glass held in  $Si(OH)_4$  is less, being only  $\approx 1/10$  of that in water. The dissolution rate of the porous glass in the first 100 h was found to be  $\approx 5 \times 10^{-4} \text{ nm/h}$  in water and  $\approx 5 \times 10^{-5} \text{ nm/h}$  in the  $Si(OH)_4$  solution. No detectable weight loss was observed for porous glass held at room temperature, even in water.

### IV. Discussion

The results in Fig. 1 show that the mechanical strength of abraded glass increased with increasing soaking time in solution at  $88^\circ C$ . This strength increase is usually explained by crack blunting caused by the dissolution of glass in water.<sup>1</sup> Alternatively, the strengthening by a surface compressive layer formation by the diffusion of water into the glass surface is conceivable. However, since the heat treatment of a water-soaked specimen at  $400^\circ C$  for 3 h, which would eliminate the possible surface compressive layer by water diffusion, did not alter the mechanical strength,<sup>4</sup> this mechanism is unlikely. Another explanation for the strength increase can be the release of the residual tensile stress produced during abrasion. Marshall and Lawn<sup>5</sup> observed that the strength of an indented soda-lime glass increases by  $\approx 20\%$  when the glass is left unstressed for  $\approx 1$  h at room temperature. They attributed this strength increase to the release of the residual tensile stress around the radial crack which determines the mechanical strength of the specimen, by the lateral crack growth. However, this residual stress effect is known to be smaller for extensively abraded samples and high-silica glass<sup>5,6</sup> specimens, which were used in the present work. Furthermore, the faster strength increase observed for specimens treated in the  $Si(OH)_4$  solution than those in water cannot be explained by the residual stress release. The fact that the strength increase was observed only when the glass dissolution rate was measurable indicates that the observed strength increase involves the dissolution of the glass and the alteration of the crack geometry.

Often the crack-tip geometry is assumed to be elliptical, as shown in Fig. 3 (solid line). The strength increase of the soaked glass indicates an increase of the radius of curvature of the crack tip. Thus it is possible to estimate the extent of the crack-tip radius change from the strength change, using the relation:

$$\sigma_1/\sigma_2 = \sqrt{\rho_1/\rho_2} \quad (1)$$

where  $\sigma_1$  is the strength of a sample with a crack-tip radius,  $\rho_1$ , and  $\sigma_2$  is the strength of a sample with a crack-tip radius,  $\rho_2$ . This equation was obtained from the Inglis equation<sup>7</sup> of stress concentration:

$$\sigma = 2\sigma_a \sqrt{C/\rho} \quad (2)$$

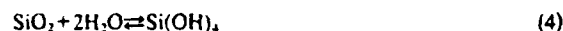
where  $\sigma$  is the stress at the crack tip,  $\sigma_a$  the applied stress (measured strength when  $\sigma$  reaches the bond strength),  $C$  the crack length, and  $\rho$  the crack-tip radius, assuming that  $C$  remains unchanged during the blunting process, i.e.

$$2\sigma_1 \sqrt{C/\rho_1} = 2\sigma_2 \sqrt{C/\rho_2} \quad (3)$$

Here, the strength change observed at liquid nitrogen temperature should be used since, at room temperature, the mechanical strength is influenced by stress rate and this stress-rate dependence changes with the soaking time.<sup>8</sup> The strength increase of glass soaked in water ( $\approx 16\%$ ) and in the  $\text{Si(OH)}_4$  solution ( $\approx 20\%$ ) for 240 h observed at the liquid nitrogen temperature, where there is no stress-rate dependence, therefore, represents the true change in crack geometry.

Crack geometry on the glass surface is not exactly known, but Pavelchek and Doremus<sup>9</sup> estimated that the crack depth is  $\approx 6 \mu\text{m}$  and the radius of curvature is  $\approx 2.0 \text{ nm}$ . Assuming an elliptical crack with these dimensions, the increase of radius of curvature was estimated from the strength increase by crack blunting. The strength increase of glass soaked in water ( $\approx 16\%$ ) and in the  $\text{Si(OH)}_4$  solution ( $\approx 20\%$ ) for 240 h corresponds to the increase of radius of curvature from 2.0 to  $\approx 2.7 \text{ nm}$  in water and to  $\approx 2.9 \text{ nm}$  in the  $\text{Si(OH)}_4$  solution. These results are summarized in Table I. These increases must be considered to occur while the glasses are held in water and the  $\text{Si(OH)}_4$  solution at  $88^\circ\text{C}$  for 240 h.

Usually, when the glass is held in water it is considered to react with, and then dissolve in, water. The chemical reaction is expressed as<sup>10</sup>



If the crack blunting, viz. the increase of radius of curvature, is due to a uniform dissolution of the glass, as shown by the dashed line in Fig. 3, the crack tip is expected to become blunt much faster in  $\text{H}_2\text{O}$  than in the  $\text{Si(OH)}_4$  solution, since the dissolution rate of the glass was found to be larger in  $\text{H}_2\text{O}$ , as shown in Fig. 2 and as expected from the chemical equation. Therefore, the strength of glass held in  $\text{H}_2\text{O}$  would be expected to increase at a faster rate than in the  $\text{Si(OH)}_4$  solution. However, the experimental result as seen in Fig. 1 shows the opposite trend. Furthermore, when the crack surface dissolves uniformly at the above rate, the radius of curvature of the crack increases only by 0.12 nm in water and 0.012 nm in the  $\text{Si(OH)}_4$  solution after 240 h, far less than expected from the strength increase. Thus, it appears unlikely that the uniform dissolution can explain the observed phenomena.

So far only the uniform dissolution of the crack surface was considered. In reality, however, the solubility is a function of curvature of the surface.<sup>11</sup> The solubility,  $S$ , of the glass surface with radius of curvature  $\rho$  is expressed as

$$\ln(S/S_0) = -(\gamma M/RT\rho) \quad (5)$$

(the glass surface has radius of curvature,  $-\rho$ ;  $\rho$  is positive)

where  $S_0$  is the solubility of the flat surface,  $\gamma$  the interface energy,  $M$  the molecular weight, and  $d$  the density of glass. Figure 4(A) shows the solubility ratio,  $S/S_0$ , of the glass as a function of  $\rho$  and  $\gamma$ , using  $M=60.1 \text{ g/mol}$ ,  $T=361 \text{ K}$ , and  $d=2.2 \text{ g/cm}^3$ ;  $\gamma$  is usually 5 to  $10 \mu\text{J/cm}^2$ .<sup>12</sup> Figure 4(B) shows the change of the radius of curvature of an elliptical crack near the crack tip. If the dissolution rate is assumed to be proportional to the solubility,  $S$ , the dissolution rate decreases rapidly with decreasing radius of curvature; at the crack tip, the dissolution rate is expected to be a minimum.

When there is a difference in dissolution rate, depending on the position in the crack, the process of dissolution and precipitation<sup>12</sup> is expected to take place, since the diffusion of dissolved glass in liquid would be reasonably high ( $\approx 10^{-5} \text{ cm}^2/\text{s}$ ).<sup>13</sup> In fact, this process was directly observed in microcracks of NaCl and KCl crystals.<sup>14</sup> The dissolution and precipitation mechanism is also used to explain the silica gel dissolution kinetics.<sup>12,15</sup> Silica precipitated from solution on a substrate is known to be dense and nonporous and similar to vitreous silica<sup>12</sup>; its strength is expected to be as high as that of high-silica glass. Thus, a more realistic model of the crack blunting would involve the glass dissolving at a portion where the radius of curvature  $\rho$  is large and precipitating at the crack tip where  $\rho$  is a minimum. The resulting crack shape by this mechanism is shown schematically by a dotted line in Fig. 3. According to this mechanism, the results in Fig. 1 can be explained reasonably: When the glass is soaked in a saturated  $\text{Si(OH)}_4$  solution, supersaturation of  $\text{Si(OH)}_4$  occurs at the crack tip where solubility is very low. Therefore  $\text{SiO}_2$  would precipitate at the crack tip, since the relation of Eq. (4) goes from right to left. As a result, at first the radius of curvature, and consequently the strength, increase rapidly. However, as the crack-tip radius of curvature increases and the degree of supersaturation at the crack tip begins to decrease (Fig. 5), the precipitation rate of  $\text{SiO}_2$  is expected to decrease. (In Fig. 5, the solubility of silica at  $88^\circ\text{C}$ , 330 ppm,<sup>16</sup> was used, since a saturated  $\text{Si(OH)}_4$  solution was used in this study.) When the degree of supersaturation became less than  $\approx 30 \text{ ppm}$ , the precipitation rate of  $\text{SiO}_2$  became very slow.<sup>17</sup> Therefore, the radius of curvature is expected to increase very little, beyond a certain value, e.g. 5 nm if the surface energy is assumed  $10 \mu\text{J/cm}^2$ . Thus, the strength increase slows down gradually and then becomes almost constant, as shown in Fig. 1. On the other hand, when the glass is soaked in  $\text{H}_2\text{O}$ , at first it dissolves at a portion with positive radius of curvature or large negative radius of curvature and the dissolved glass diffuses into the crack and then precipitates at the crack tip. Therefore, the strength increase of the glass soaked in water is slower than that in the  $\text{Si(OH)}_4$  solution. At room temperature, since both the dissolution rate and the precipitation rate of  $\text{SiO}_2$  are considered to be very low, the mechanical strength increase is expected to be very small in both water and the  $\text{Si(OH)}_4$  solution.

Thus, precipitation-dissolution appears to be the mechanism of crack blunting of high-silica glass.

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**At a wedge crack**

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<sup>14</sup>7900 Vycor Glass, Corning Glass Works, Corning, NY.  
<sup>15</sup>Custom-made at Owens-Illinois Technical Center, Toledo, OH.  
<sup>16</sup>Measured by Microchemics, Norcross, GA.

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Table I. Strength of High-Silica Glass at Liquid N<sub>2</sub> Temperatures and Estimated Radius of Curvature

Sample	Strength in liquid N <sub>2</sub> (MPa)	Increase of strength after treatment (%)	$\rho$ (nm)
Freshly abraded	134 ± 10		≈ 2.0
Soaked in H <sub>2</sub> O at 88°C for 240 h	155 ± 7	≈ 16	≈ 2.7
Soaked in Si(OH) <sub>4</sub> solution at 88°C for 240 h	161 ± 9	≈ 20	≈ 2.9

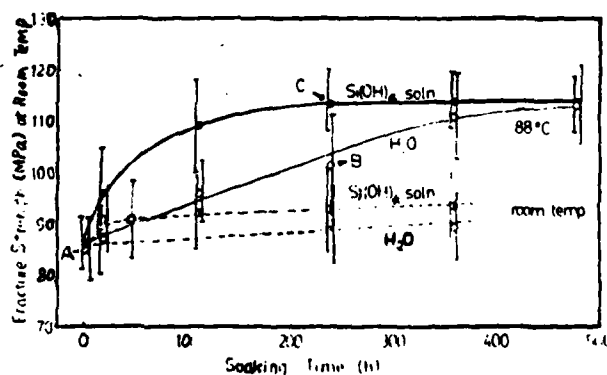


Fig. 1. Fracture strength of high-silica glass rod at room temperature as a function of soaking time (○) in H<sub>2</sub>O at 88°C, (○) in H<sub>2</sub>O at room temperature, (●) in Si(OH)<sub>4</sub> solution at 88°C, and (○) in Si(OH)<sub>4</sub> solution at room temperature. (Strength of specimen soaked in water was measured in water and that of specimen soaked in Si(OH)<sub>4</sub> solution in Si(OH)<sub>4</sub> solution; error bars indicate ±1 standard deviation.)

was measured

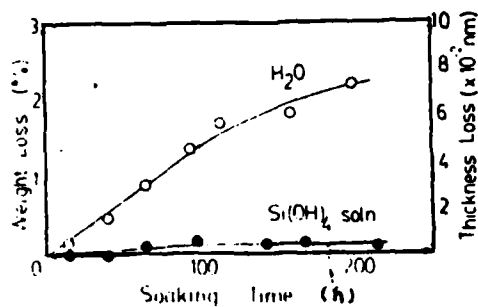


Fig. 2. Dissolution rate of high-silica porous glass in H<sub>2</sub>O and Si(OH)<sub>4</sub> solution at 88°C.

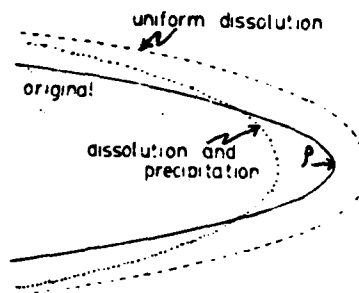


Fig. 3. Schematic of crack-tip geometry.

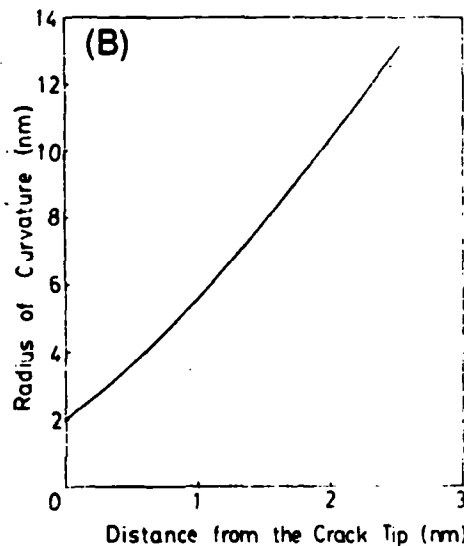
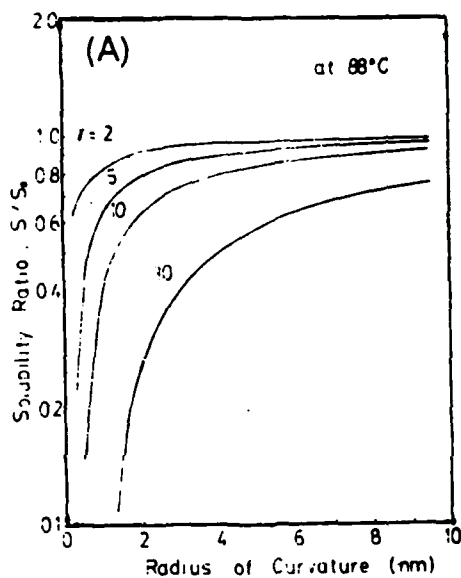


Fig. 4. (A) Solubility ratio at 88°C as a function of radius of curvature of crack surface.  $S$  = solubility of ~~the~~ <sup>the glass</sup> surface at a crack with radius of curvature,  $\rho$ , and  $S_0$  = solubility of flat surface;  $\gamma$  is given in  $\mu\text{J}/\text{cm}^2$ . (B) Radius of curvature near crack tip as a function of distance (in direction of crack) from crack tip, assuming an elliptical crack 6  $\mu\text{m}$  deep with crack-tip radius 2 nm.

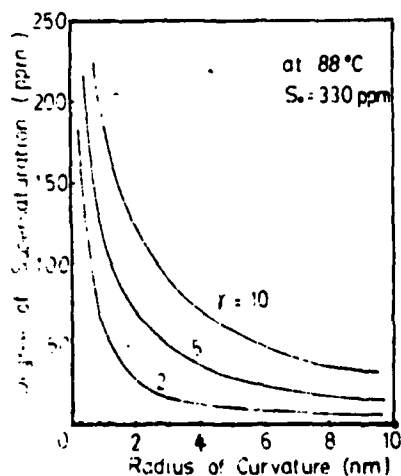


Fig. 5. Degree of supersaturation as a function of radius of curvature of crack ~~surface~~;  $\gamma$  is given in  $\mu\text{J}/\text{cm}^2$ .



**APPENDIX E**

EFFECTS OF SURFACE CONDITIONS ON STRESS-RATE DEPENDENCE OF  
MECHANICAL STRENGTH OF HIGH SILICA GLASS

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Changing the surface conditions of high silica glass was found to influence the stress rate dependence of mechanical strength. Specifically, the replacement of hydroxyl groups on the glass surface with silane or Grignard reagent nearly completely eliminated stress rate dependence and the soaking treatment in water at 88°C reduced the stress-rate dependence. The results appear to be inconsistent with the stress-corrosion mechanism. Instead they can be explained in terms of the reduction of the surface energy as a function of time.

INTRODUCTION

Mechanical strength of glass is known to depend upon the stress rate of the measurement.<sup>1-4</sup> This phenomenon, sometimes called a dynamic fatigue, is believed to be closely related to the static fatigue and is usually explained in terms of the stress-corrosion mechanism.<sup>1</sup> Namely, it is believed that the glass corrosion reaction accelerated by a tensile stress reduces the glass strength and that in the higher stress-rates, the glass surface has little time to undergo the corrosion reaction with water or water vapor and so the glass tends to show a higher mechanical strength. However, a similar stress-rate dependence was found for the mechanical strength of high silica glass measured in liquid  $\text{CCl}_4$ ,<sup>5</sup> as well as in water even though the former does not react with glass. At a constant stress rate, the mechanical strength of high silica glass measured in various liquids correlated well with the surface energy of the glass in the liquid.<sup>5,6</sup> Furthermore, direct measurement of the corrosion rate of glass under hydrostatic pressure showed an increase in the corrosion rate with compressive stress,<sup>7</sup> contrary to what is expected from the

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stress-corrosion hypothesis. These observations led the present authors to an alternative mechanism, i.e. time dependent surface energy at the crack tip. Since the lower surface energy leads to the lower mechanical strength, the gradual reduction of the surface energy can account for the lowering of the strength of time, i.e. fatigue.

The surface energy of the glass can be reduced by the adsorption, both chemical and physical, of various molecules. In the case of water-glass interaction, chemical adsorption produces the surface hydroxyl and physical adsorption of molecular water takes place preferentially at these surface hydroxyl sites.<sup>8</sup> Other molecules such as benzene are also known to be physically adsorbed on the surface hydroxyl.<sup>9</sup> Thus it is expected that if the surface hydroxyl is eliminated from the glass surface, physical adsorption of molecules becomes difficult and consequently reduction of the surface energy will be hampered. According to the mechanism suggested by the present authors, this type of surface would lead to the reduction of the fatigue phenomenon. Alternatively, when the surface energy is reduced such that very little additional reduction can take place, the fatigue should be minimized. With these ideas, the effects of the surface conditions on the stress-rate dependence of high silica glass were investigated. Specifically, in order to prevent the physical adsorption of water, chemical treatment was given whereby the surface hydroxyl is replaced by other radical. Alternatively, in order to minimize the additional surface energy reduction, glass was soaked in water at the temperature where crack tip is known to react with water.

There are several previous investigations<sup>10-12</sup> on the surface treatment-fatigue relation of various commercial glasses such as soda-lime glass. Here, in order to avoid the possible complications caused by alkali ion-water reaction, a high silica glass with low alkali concentration is used.

#### EXPERIMENTAL

Commercial high silica glass rods\* ( $\sim 3$  mm in diameter; 6 cm in length) were used for the measurement. The surface of the glass rods was abraded by tumbling 60 glass rods with 100 g of silicon carbide powder (600 grit) for 2 hrs in a 1 l jar mill. After abrasion the samples were washed three times in an ultrasonic cleaner for 2 minutes each time in water and then dried at 120°C for about 3 hrs in an oven. Subsequently, the samples were immersed in various liquids for surface treatment of the samples at least 2 hrs. The liquids employed were

- (a) water
- (b) 2 vol %  $\text{CH}_3\text{SiCl}_3$  in Heptane solution
- (c) 2 vol %  $(\text{CH}_3)_3\text{SiCl}$  in Heptane solution
- (d) 0.1 M  $\text{CH}_3\text{MgBr}$  (Grignard reagent) in n-Buthyl ether solution

\* Corning 7900, Corning Glass Works, Corning, New York.

$\text{CH}_3\text{SiCl}_3$ ,<sup>13</sup>  $(\text{CH}_3)_3\text{SiCl}$ <sup>13</sup> and  $\text{CH}_3\text{MgBr}$ <sup>14</sup> in liquids (b), (c), and (d), respectively, are known to react with hydroxyl groups on the glass surface and water in the liquids, thus removing water in the environment. (In order to accelerate the reaction between the glass surface hydroxyl and silane, the specimen was pre-treated in the respective silane solution containing 1 vol %  $(\text{C}_2\text{H}_5)_3\text{N}$  before they are placed in the above silane solution). The resulting glass surfaces in (b) and (c) are known to be hydrophobic.<sup>15</sup> Water (a) was used for reference purpose.

Other groups of abraded glass rods were soaked in water at 88°C for 112 and 240 hrs, respectively, prior to the mechanical strength measurement in water at room temperature. These soaking treatments increase the mechanical strength by approximately 10% by the process of crack blunting.<sup>16</sup>

The mechanical strength of the glass rods were measured in liquids, (a)-(d), at room temperature in dry  $\text{N}_2$  by the four point bending method. Stress rates of  $9.6 \times 10$ ,  $4.8 \times 10^2$ ,  $9.7 \times 10^2$ ,  $9.2 \times 10^3$ ,  $4.6 \times 10^4 \text{ kg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$  were used. At least 10 specimens were used for strength measurement at each stress rate in a given environment. For selected specimens, the strength in liquid  $\text{N}_2$  was also measured at constant stress rate,  $9.2 \times 10^3 \text{ kg}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ . In this case, measurement was made for at least 22 specimens.

## RESULTS

In Fig. 1, the stress-rate dependence of the mechanical strength of the high silica glass in various liquids are shown. The stress rate dependence was evaluated using the expression derived by Charles,<sup>1</sup> namely

$$\sigma = K \beta^{\frac{1}{n+1}} \quad (1)$$

where  $\sigma$  is the strength,  $K$ , is a constant,  $\beta$  is the stress rate and  $n$  is a parameter related to the slope of  $\log \sigma$  vs.  $\log \beta$ . This equation (1) was originally derived from the hypothesis that the crack extends by stress-corrosion and the crack extension rate is proportional to the  $n$ th power of the stress at the crack tip. But, here,  $n$  is used simply as a measure of the stress rate dependence of the strength. From the results in Fig. 1, it is clear that the high stress rate dependence (low  $n$  value) which is usually observed in water or air, is eliminated almost entirely when measured in  $(\text{CH}_3)_3\text{SiCl}$  or  $\text{CH}_3\text{MgBr}$  (Grignard reagent) solution while it remains practically unchanged in  $\text{CH}_3\text{SiCl}_3$  solution. In  $\text{CH}_3\text{SiCl}_3$ , the strength is extremely high at high stress rate.

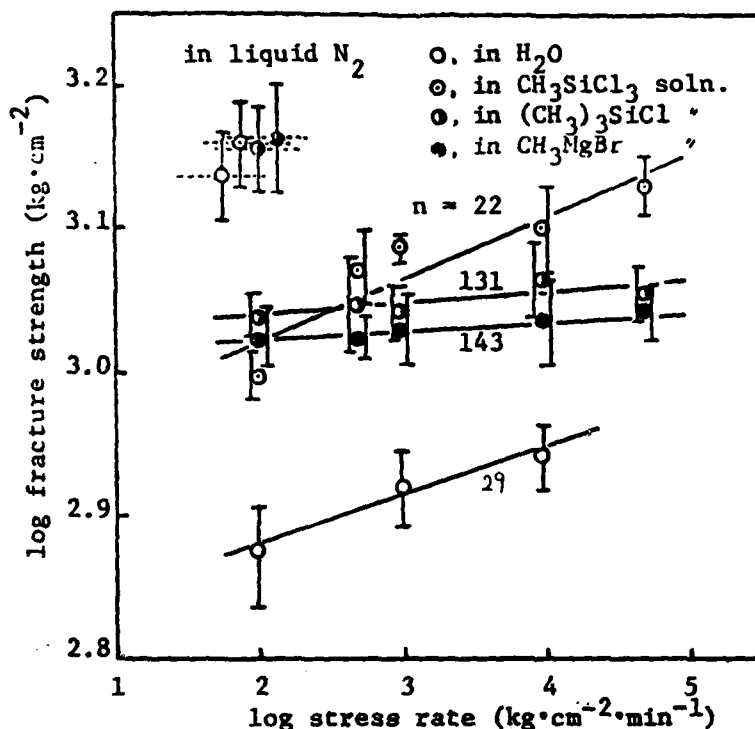


Fig. 1 Stress rate dependence of fracture strength of high silica glass rod in various liquids at room temperature. The error bar indicates  $\pm 1$  standard deviation.

In this figure, the strengths of the glass measured in liquid nitrogen are also indicated. The strengths of the glass treated by silane and Grignard reagent were almost the same and were slightly higher than that of freshly abraded glass.

In order to confirm that the observed strength variation in different liquids was not caused by a permanent damage of the surface, e.g. crack extension, a specimen treated in Grignard reagent ((c) in Table 1) was dipped in water to produce the surface hydroxyl and then its strength was measured in liquid  $N_2$  and in  $CH_3SiCl_3$  solution. As shown in Table 1, the observed strengths in liquid  $N_2$  (d) and in  $CH_3SiCl_3$  solution (e) were nearly equal to the original values in liquid  $N_2$  (a) and in  $CH_3SiCl_3$  solution (b). These results indicate that the surface treatments given here are reversible.

In Fig. 2, the effects of soaking the abraded glass rods in water at  $88^\circ C$  for various lengths of time on the strength in water at room temperature are shown. It is known that this soaking treatment in general increases the strength of glass and the phenomenon is usually explained in terms of the crack blunting.<sup>17</sup> Figure 2 shows that, in

Table 1. Effect of Surface Treatment on Permanence of Surface Damage

Treatment	Fracture Environment	Fracture Strength* (kg·cm <sup>-2</sup> )
(a) freshly abraded	liquid N <sub>2</sub>	1370 ± 99
(b) immersed in CH <sub>3</sub> SiCl <sub>3</sub> soln after treatment (a).	CH <sub>3</sub> SiCl <sub>3</sub> soln	1260 ± 88
(c) immersed in CH <sub>3</sub> MgBr soln after treatment (a).	CH <sub>3</sub> MgBr soln	1080 ± 76
(d) immersed in H <sub>2</sub> O after treatment (c).	liquid N <sub>2</sub>	1400 ± 110
(e) immersed in CH <sub>3</sub> SiCl <sub>3</sub> soln after treatment (d).	CH <sub>3</sub> SiCl <sub>3</sub> soln	1210 ± 87

\* measured at  $9.2 \times 10^{-3}$  kg·cm<sup>-2</sup>·min<sup>-1</sup>  
 ±1 Standard Deviation

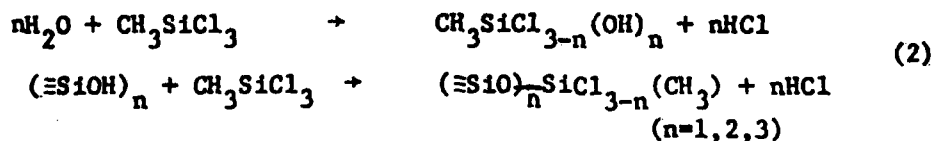
addition to the strength increase, the stress rate dependence of the strength also changes by the soaking treatment, the strength becoming less sensitive to the stress rate as the soaking (or crack blunting) increases. In the figure, the strengths measured in liquid N<sub>2</sub> are also indicated, both for the freshly abraded specimen and the soaked specimen.

#### DISCUSSION

There are several previous investigations on the effect of the surface conditions on the dynamic fatigue behavior of high silica glass. They are summarized in Table 2, where n values, a measure of the fatigue susceptibility (the smaller n indicates that the strength is more sensitive to the stress rate), are shown for high silica glass. From this table, it can be seen that most of the n values obtained by the previous investigators are approximately the same (being in the range of 20-40) except for Al coated glass, by Pinnow,<sup>23</sup> which does not show any fatigue.

On the other hand, in the present study, much larger n values were obtained

Chemicals used in this study can readily react with water and can remove both chemically adsorbed water and physically adsorbed water from glass surface as well as from the solvent. The chemical reactions can be expressed as follows:<sup>13,14</sup>



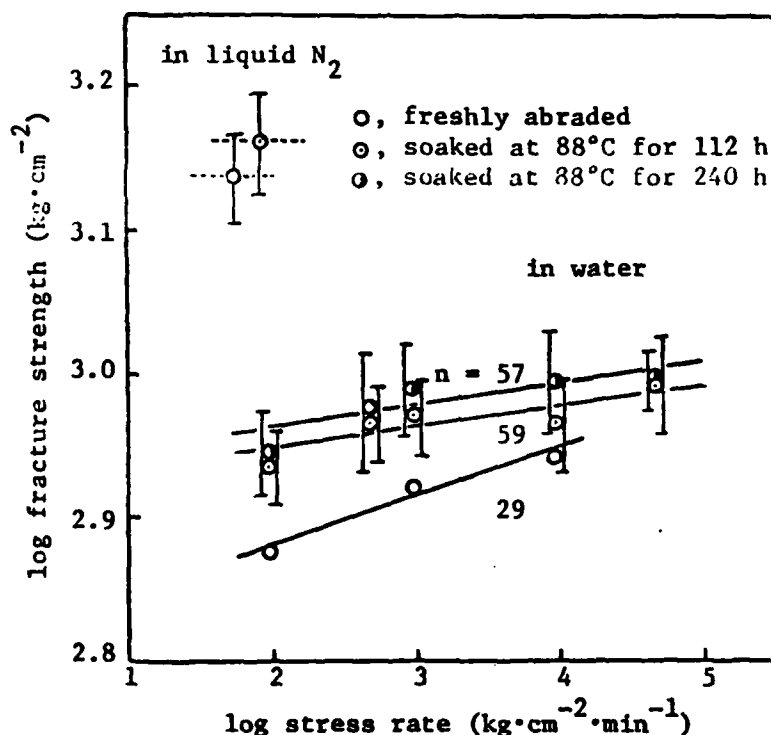
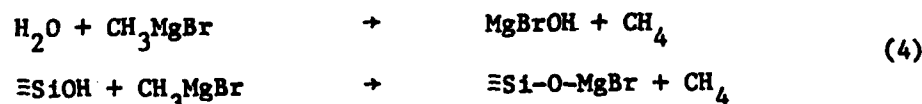
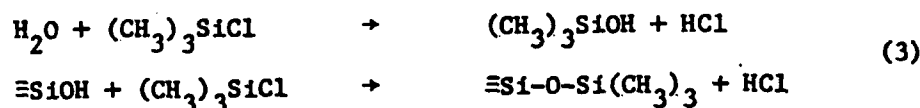


Fig. 2 Stress rate dependence of fracture strength of soaked and freshly abraded high silica glass in water at room temperature. The error bar indicates  $\pm 1$  standard deviation.



The first reaction in each set of equations (2), (3), and (4), represents the reaction between the chemical and free water on the glass surface as well as in the solvents, while the second one represents the reaction between the chemical and the glass surface hydroxyl. In this study, after treating the surface with  $(\text{CH}_3)_3\text{SiCl}$  and  $\text{CH}_3\text{MgBr}$  solutions, the stress rate dependence of the glass strength became very small while it did not change significantly in the  $\text{CH}_3\text{SiCl}_2$  solution. The reasons considered are that in  $(\text{CH}_3)_3\text{SiCl}$  and  $\text{CH}_3\text{MgBr}$  solution, water on the glass surface as well as in the solvent is

Table 2. Stress-rate Dependence of Mechanical Strength (n value) for High Silica Glass

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Sample	Environment	Surface Coating	n	Ref.
Abraded rod	wet	none	37.8	18
Abraded fiber	water	none	37.5	19
As drawn fiber	50% RH	none	18.5~32	4,20,21
As drawn fiber	45~90% RH	Epoxy Acrylate	20	22
As drawn fiber	2~97% RH	Ethylene Vinyl Acetate	16~29	4
As drawn fiber		Al	No Fatigue	23
Abraded rod (96% SiO <sub>2</sub> )	CCl <sub>4</sub>	none	21	5
Abraded rod (96% SiO <sub>2</sub> )	water	none	29	Present Study
	CH <sub>3</sub> SiCl <sub>3</sub> +C <sub>7</sub> H <sub>16</sub>	(-O) <sub>n</sub> Si(CH <sub>3</sub> )Cl <sub>3-n</sub>	22	
	(CH <sub>3</sub> ) <sub>3</sub> SiCl+C <sub>7</sub> H <sub>16</sub>	-O-Si(CH <sub>3</sub> ) <sub>3</sub>	131	
	CH <sub>3</sub> MgBr+(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> O	-O-MgBr	143	
	water after soaking	none	59	

almost completely removed by the above chemical reactions, but not in the CH<sub>3</sub>SiCl<sub>3</sub> solution. CH<sub>3</sub>SiCl<sub>3</sub> can react with CH<sub>3</sub>Si(OH)<sub>n</sub>Cl<sub>3-n</sub> (n=1,2,3) produced by the reaction of CH<sub>3</sub>SiCl<sub>3</sub> with water and polymerize,<sup>24</sup> forming a polymer coating on the glass surface.<sup>15</sup> As a result, some physically adsorbed water and chemically adsorbed water remain unreacted on the surface. This remaining water is probably affecting the stress rate dependence of the strength.

Thus, the almost complete removal of physically and chemically adsorbed water as well as water in the solvent as in (CH<sub>3</sub>)<sub>3</sub>SiCl or CH<sub>3</sub>MgBr solution give much larger n values, but an incomplete removal of water as in CH<sub>3</sub>SiCl<sub>3</sub> solution, does not give a large n value.<sup>5</sup> This latter result appears similar to the result obtained in CCl<sub>4</sub>,<sup>5</sup> where the surface hydroxyl on the glass surface was not removed.

On the other hand, as shown in Fig. 2 and Table 2, after glasses were soaked in water at 88°C for extended periods of time, the n value of the glasses became larger than that of freshly abraded glass. The soaked specimen is stronger at liquid N<sub>2</sub> temperature, also indicating that the crack blunting is taking place.<sup>16</sup>

These observations will first be compared with the stress-corrosion mechanism. In this mechanism, the corrosion velocity, v, is considered to be accelerated by the tensile stress  $\sigma_m$  at the crack tip by the following equation<sup>1</sup>



$$v = k(\sigma_m)^n e^{-A/RT} \quad (2)$$

where  $k$ ,  $A$ ,  $n$  are constants and  $R$  and  $T$  have the usual meanings. When equation (2) is combined with Inglis' expression<sup>25</sup> for stress concentration

$$\sigma_m = 2\sigma_a \sqrt{\frac{c}{\rho}} \quad (3)$$

where  $\sigma_a$  is the applied stress,  $c$  is the crack length and  $\rho$  is the crack tip radius and the stress rate equation is

$$\sigma_a = \beta t \quad (4)$$

where  $\beta$  is the stress rate and  $t$  is time, knowing  $v = \frac{dc}{dt}$ , equation (1) can be derived. The constant  $K$  in equation (1), is, therefore, given by

$$K = \left[ \frac{n+1}{\frac{n}{2}-1} \left(\frac{1}{k}\right) e^{A/RT} \left(\frac{\rho}{2}\right) C_0^{1-\frac{n}{2}} \right]^{\frac{1}{n+1}}$$

where  $C_0$  is initial crack length. The parameters  $K$ , and in some cases  $\rho$  and  $c$ , can, in general, be altered by the surface treatment but the value of  $n$  is expected to be independent of the surface treatment. According to this mechanism, therefore, the lines in Figures 1 and 2 are expected to shift parallel maintaining the nearly same  $n$  value. One of the striking features of the present result is that lines in Figure 1 cross over. If the stress-rate dependence is due to stress-corrosion, when the same glass composition and the reversible surface treatment are used, the crossing of the two lines are not expected. Even if the surface modification influences the stress rate dependence, according to the stress corrosion mechanism, the high strength is obtained by the absence or the slow rate of the corrosion reaction and should be associated with the larger  $n$  value while the lower strength is caused by the higher corrosion susceptibility (low  $n$  value). Thus the observed results are inconsistent with the stress-corrosion mechanism.

Next, the observed results are compared with the surface energy mechanism recently proposed by the present authors<sup>26</sup>. The glass surface treatment with  $(CH_3)_3SiCl$  or with  $CH_3MgBr$  replaces the surface hydroxyl,  $OH$ , with  $-OSi(CH_3)_3$  or  $-OMgBr$ . At the same time, the impurity water in the solvents is also eliminated. Unlike the surface hydroxyl, adsorption of solvent molecules on these surface groups is difficult and therefore, very little surface energy reduction by

adsorption is expected, thus the  $n$  values are larger.

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The absence of the stress-rate dependence in Al coated fiber glass observed by Pinnow<sup>23</sup> may be explained in a similar manner. When a freshly drawn glass fiber is coated with a metal such as Al at a high temperature before surface hydroxyl is formed, the surface is probably covered by  $-OAl$ , which may be acting similarly to the radical formed by the present treatments.

Different strength, at a given stress rate, for different surface treatments would probably correspond to the resultant surface energy of glass, as was demonstrated previously by measuring the mechanical strength of high silica glass in various solvents.<sup>6</sup>

When the abraded glass is soaked in water at 88°C, the phenomenon of crack blunting takes place indicating that the water had sufficient time to interact with the glass surface at the crack tip. Dissolution of glass, and chemical as well as physical adsorption of water would take place at the crack tip during this treatment. Since very little additional reduction of the surface energy can take place by adsorption, a large  $n$  value is expected. The experimental results confirm this expectation giving a large  $n$  value. However, a finite stress-rate dependence is remaining. This may be explained as follows: When the glass is kept in a 100% humidity atmosphere the glass surface is covered by the physically adsorbed water, and the surface energy is reduced. Additional surface energy reduction takes place when the glass is dipped in water.<sup>27</sup> These phenomena suggest that the thickness of the adsorbed water molecule layer has an influence on the surface energy. When a thin crack is exposed to water, the amount of water which can wet the crack tip is limited. As the crack is opened by the externally applied stress, the additional water can enter the crack tip reducing further the surface energy of the crack tip. This phenomenon can account for the finite stress-rate dependent strength observed for the soaked specimens.

The magnitude of the strength is higher here for the soaked specimen since crack blunting has taken place as indicated by the increased strength at liquid  $N_2$  temperature.

Thus the observed experimental data appear consistent with the idea that the time dependent mechanical strength of glass is related to a time dependent surface energy of the glass.

#### ACKNOWLEDGEMENT

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